

UV-CURING ANTI-FINGERPRINTING COATINGS

5 This application is a continuation under 35 USC Sections
365(c) and 120 of International Application No.
PCT/EP02/09967, filed 6 September 2002 and published 20 March
2003 as WO 03/022945, which claims priority from German
Application No. 10144531.8, filed 11 September 2001, each of
10 which is incorporated herein by reference in its entirety.

Field of the Invention

The present invention relates to a process for producing
stain-resistant function coatings for metal surfaces, in
15 particular aluminum or high-grade steel surfaces, as well as
suitable coating materials for these.

Discussion of the Related Art

A multitude of appliances, equipment and machines made of
20 metal, in particular high-grade steel or aluminum, are used in
households, in sanitary applications, in hospitals as well as
in the food-processing and pharmaceutical industries. Here,
owing to its high resistance to corrosion, e.g. high-grade
steel is preferably used. This is frequently used with a
25 polished or brushed surface and without additional coatings.
Furthermore, a multitude of metallic parts having very
different compositions are also used in architecture, for
interior fittings of buildings, in furniture-making as well as
for ornamental applications. In these cases, too, the surface
30 of the metal is frequently polished, brushed or otherwise
provided with surface patterns and is used without the
application of further coatings.

In this form, the metal surface is highly susceptible to
35 soiling by dust, food or cleaning agents, or marking by
fingerprints. A number of methods of treating the surfaces of
metals in order to improve the scratch resistance of the
surface or to avoid soiling have already been proposed. These

involve coating processes using solvent-based and aqueous systems, for example, aqueous electrophoretically precipitable dip coatings, or powder coatings. These coatings are intended to improve the soiling behavior and the scratch resistance of the surface. Disadvantages of the processes are, for example, the curing conditions, such as time, temperature, as well as the consequent plant dimensions. Moreover, it is frequently impossible to form the objects without destroying the surface coating.

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DE 199 57 325 and DE 199 52 323 describe coating materials for metals or plastics; there the coating materials are heat-curable and based on aqueous sols consisting of organosilicon compounds. EP 1 036 829 deals with UV-cross-linkable coating materials for metals and conductive plastics, but describes only aqueous systems, which are applied to electrically conducting substrates by means of electrophoretic coating and are subsequently first of all dried at elevated temperature, then post-cured under UV light.

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JP-A-07/171496 and JP-A-04/150976 (1992) describe heat-curable coatings on high-grade steel which are produced from polyester resins and silicate resin or melamine resin. JP 10/228446 and EP 0 789 065 describe special UV-cross-linking coating systems substantially for coating wood, which are applied in layers of above 20 or 30 μm .

Although, therefore, there exists an extensive prior art concerning UV-cross-linking coating materials, the problem of coating with thin layer thicknesses in order to avoid soiling of metal or even of plastics substrates has not yet been solved. In this connection, the coated surface should have a good stain resistance and be scratch resistant; in addition, the natural appearance in particular of brushed or otherwise structured metal surfaces should be preserved. No observations about these requirements are made in prior art. Furthermore, an energy-saving, rapid and environmentally mild coating

process is required, in order to be able to coat even large surfaces economically. A further requirement is that it should be possible to form the coated objects without impairing the coating. The object, therefore, was to provide for these
5 purposes a solvent-free, thin coating system having a high scratch resistance and chemical resistance to alkaline and acidic cleaning agents, such as are used in households and in commerce or in the food-processing industry.

10 Brief Summary of the Invention

According to the invention, this object is achieved by the provision of a solvent-free liquid coating material which is cross-linked by means of high-energy radiation and, within a temperature range of 0 to 90°C, preferably 15 to 70°C, has a
15 viscosity of less than 1000 mPas, containing

- a) 40 to 90 wt.% of at least one oligomeric, linear or branched epoxy (meth)acrylate, polyester (meth)acrylate, polyether (meth)acrylate and/or urethane (meth)acrylate,
- b) 5 to 60 wt.%, preferably 10 to 60 wt.%, of at least one
20 monofunctional liquid (meth)acrylate or di-, tri- or poly(meth)acrylate compound, and
- c) 0.1 to 20 wt.% of methacrylate compounds containing acidic groups,
- d) optionally 0 to 30 wt.% of a di- or trialkoxysilane
25 containing further functional groups,
- e) 0.1 to 20 wt.% of auxiliary substances used in coating technology, such as adhesion promoters, flow-control agents, defoaming agents and/or light stabilizers as well as photoinitiators.

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The coating material according to the invention is used preferably as coating material for metallic surfaces having thin coatings which are resistant to hydrolysis and to cleaning agents and are scratch resistant. The invention also
35 provides the use of the coating material according to the invention, where the coating material is rendered antibacterial.

The invention also provides a process for coating metallic surfaces, wherein the substrate is optionally first of all cleaned and degreased, the coating material according to the invention is then applied in a layer thickness of 0.5 to 20 μm and finally the coating is cross-linked by means of high-energy radiation. The invention further provides a process for coating those surfaces wherein, prior to the cross-linking step, the coated surface is provided with a removable protective coating film.

Detailed Description of Certain Embodiments of the Invention

The process according to the invention and the coating material according to the invention are particularly suitable for use on surfaces consisting of ferrous materials, steel and alloyed steel, light metals such as aluminum, magnesium, titanium, non-ferrous metals such as copper, zinc, tin, or precious metals such as gold, silver or alloys thereof. This surface may be ground, brushed, polished, electrochemically treated or electrolytically coated, for example, cadmium-plated, chromium-plated or nickel-plated. Metallized plastics surfaces are also suitable. The substrate may have any shape, but is preferably in the form of sheets, strips or rolls.

The coating materials according to the invention contain polymerizable oligomers containing unsaturated double bonds such as, for example, polyester oligomers or polyether oligomers having lateral or terminal (meth)acrylic groups, or preferably (meth)acrylate functional aliphatic, cycloaliphatic and/or aromatic epoxide compounds or polyurethane oligomers having reactive (meth)acrylate groups. These oligomers are to have at least two functional unsaturated double bonds and in general have a molecular weight of between 500 and 15000. They are obtainable commercially. The quantity is 40 to 90 wt.%, in particular 45 to 85 wt.%, and mixtures of different oligomers are also possible.

The coating material is also to contain at least one mono-, di-, tri- or polyfunctional unsaturated low-molecular (meth)acrylate, with separate compounds or mixtures possibly being present. Examples of such compounds are: optionally

5 alkoxyated alkanediol (meth)acrylates or alkanetriol (meth)acrylates, such as 1,3-butylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, trialkylene glycol di(meth)acrylate, polyalkylene glycol di(meth)acrylate, tetraalkylene glycol

10 di(meth)acrylate, neopentyl glycol di(meth)acrylate, glycerol alkoxytri(meth)acrylate, alkoxyated neopentyl glycol di(meth)acrylate; (meth)acrylic epoxide compounds, such as bisphenol A epoxide di(meth)acrylate; polyhydroxy (meth)acrylates, such as pentaerythritol tri(meth)acrylate,

15 trimethylolpropane tri(meth)acrylate, trisalkoxy-trimethylolpropane tri(meth)acrylate, di-trimethylolpropane tetra(meth)acrylate, pentaerythritol tetra(meth)acrylate, tris(2-hydroxyalkyl) isocyanurate tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate, dipentaerythritol

20 penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, with alkylene denoting ethylene, propylene or butylene and alkoxy denoting ethoxy, 1,2- or 1,3-propoxy or 1,4-butoxy.

The following (meth)acrylates are examples of monofunctional

25 acrylate compounds which can be used: linear, branched or cyclic alkyl (meth)acrylates, such as n-/isoalkyl (meth)acrylate, cyclohexyl (meth)acrylate, 4-tert.-butyl cyclohexyl (meth)acrylate, dihydrocyclopentadienyl (meth)acrylate, tetrahydrofurfuryl

30 (meth) acrylate, isobornyl (meth)acrylate, allyl (meth)acrylate, mono(meth)acryloyl alkyl phthalate, succinate or maleate; alkanediol mono(meth)acrylates, such as hydroxypropyl (meth)acrylate, polyalkylene glycol (meth)acrylate, monoalkoxytrialkylene glycol (meth)acrylate,

35 2,3-epoxypropyl (meth)acrylate; aromatic (meth)acrylates, such as nonylphenol (meth)acrylate, 2-phenoxyalkyl (meth)acrylate; acrylamides, such as

N,N-dialkyl (meth)acrylamide, N,N-dialkylaminoalkyl (meth)acrylamide. A proportion of vinyl ethers may also be used, for example, vinyl ethyl ether, vinyl propyl ether, vinyl isobutyl ether, vinyl dodecyl ether, butanediol-1,4-
 5 divinyl ether, diethylene glycol divinyl ether, hydroxybutyl vinyl ether. The monomeric acrylate compounds may be present separately or as a mixture, the total quantity amounting to between 5 and 60 wt.%, in particular between 15 and 50 wt.%.

10 The coating materials may also contain di- or trialkoxysilanes having additional organofunctional groups. Examples of these are aminopropyltrialkoxysilane, bis(trialkoxysilylpropyl)amine, hydroxyethyl-trialkoxysilane, carboxypropyltrialkoxysilane, vinyltrialkoxysilane, with
 15 alkoxy in each case denoting methoxy, ethoxy, propoxy or butoxy. The quantity is to be preferably between 0 and 15 wt.%.

Preferably, the coating materials are to contain methacrylate
 20 compounds which have acidic groups and contain one, two or more (meth)acrylic groups and in addition acidic functional groups. The quantity of this component is to be between 0.1 and 20 wt.%, preferably between 0.5 and 10 wt.%. Examples of such acidic functional groups are carboxyl groups, phosphoric
 25 or phosphonic groups, sulfo groups and derivatives thereof, for example, esters. Phosphoric groups are particularly preferred.

The known, preferably radical, initiators can be used as
 30 photoinitiators, such as, for example, 2-benzoyldimethylamino-1-(4-morpholinophenyl)butanone-1, benzil dimethylketal or dimethoxyphenylacetophenone, α -hydroxybenzyl phenyl ketone, 1-hydroxy-1-methylethyl phenyl ketone, oligo-2-hydroxy-2-methyl-1-(4-(1-
 35 methylvinyl)phenyl)propanone, benzophenone, methylorthobenzoyl benzoate, methyl benzoyl formate, 2,2-diethoxyacetophenone, 2,2-di-sec.-butoxyacetophenone,

p-phenylbenzophenone, 2-isopropylthioxanthone,
2-methylantraquinone, 2-ethylantraquinone,
2-chloroantraquinone, 1,2-benzantraquinone, benzil, benzoin,
benzoin methyl ether, benzoin isopropyl ether,
5 α -phenylbenzoin, thioxanthone, diethylthioxanthone,
1,5-acetonaphthalene, 1-hydroxycyclohexyl phenyl ketone, ethyl
p-dimethylaminobenzoate. These may be used separately or as a
mixture or combined with other radical initiators of the
peroxide type or with amine accelerators.

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Besides the above-mentioned binders, the coating material
according to the invention contains small quantities of other
additives which have a beneficial influence on, for example,
the flow properties, film formation, adhesion or resistance of
15 the coating material. Examples of these are flow-control
agents, such as fluorinated polysilicone glycols, silicone
glycols, polyether polysiloxane copolymers. The known agents
based on sterically hindered amino compounds can be used as
light stabilizers.

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The coating material may also contain dyes, optical
brighteners and/or pigments as additives. Dyes are those based
on organic dyes, which are soluble in the coating material.
These form colored transparent coatings after the film has
25 cured, and together with the substrate surface can produce
special visual effects. Optical brighteners are compounds of
the type which absorb UV radiation and reradiate it in visible
light; they may, for example, be selected from among the
triazine derivatives. By pigments are meant organic or
30 inorganic, colored or uncolored pigment preparations, such as
iron oxide pigments, titanium dioxide pigments, carbon black,
quinacridone or phthalocyanine pigments. These have to be
homogeneously distributed in the coating material. In this
connection, the particle size has to be appreciably less than
35 the intended layer thickness, preferably less than 1 μm . It
may be advantageous to disperse these components in portions
of the liquid acrylate compounds prior to addition to the

coating material.

Micronised fillers such as, for example, silica, aluminum oxide, titanium dioxide or barium sulfate, may also be used.

5 These are white, colorless or opaque/transparent and are used in finely dispersed form. Depending on quantity and type, they can influence the surface hardness, structure and scratch resistance of the coating. The quantity of auxiliary substances is to be between 0.1 and 20 wt.%, preferably 0.5 to 10 15 wt.%.

Moreover, in a preferred embodiment the coating material may contain antibacterial or biocidal compounds. These are, for example, organic substances, such as bioguanidines, 15 substituted benzalkonium halides, alkyl polyvinylpyridines, betaine, or inorganic compounds, such as silver salts or finely divided silver particles within the particle-size range of a few nm. The quantity is to be 0.1 to 5 wt.% and depends on the activity of the substance used. These compounds are 20 incorporated into the coating material and are not destroyed during the cross-linking reaction. They result in surfaces having long-term antibacterial action.

The components of the coating material according to the 25 invention can be mixed together by means of known methods. Here, it may be useful to dissolve or, for example, in the case of pigments, to disperse solid components in components of low viscosity. To ensure stability in storage, in the case of particularly reactive components it may be beneficial to 30 premix these in components of low viscosity prior to addition to the coating material and limit a possible reaction.

The process according to the invention can be adapted for the objects to be coated in the process. Depending on the 35 condition of its processing, the substrate is subjected to a cleaning step, which can be carried out by dipping, spraying, high-pressure or injection spraying or with the assistance of

ultrasound or electrolysis. In the course of this, dust particles, oxide layers, adhering residues or fatty/oily substances are removed from the production process. The known, preferably aqueous, cleaning agents can be used for the
5 cleaning process. After the cleaning process, the surface is rinsed with water, dried and then immediately further processed. Preferably, no further pretreatment is carried out prior to the coating with the coating material according to the invention; in particular, no primer is applied.

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The substrate can be covered with the coating material by means of the known methods of application. If formed or profiled parts are to be coated, mainly the spraying systems commonly used in coating technology, such as, for example,
15 airless, air-assisted or electrostatically assisted spraying processes, are suitable, or even manual application by brush. Particularly preferably, the coating material is applied to a level surface of a workpiece or of a metal strip by flooding/squeezing off, spraying/
20 squeezing off, or by suitable squeegee or roller applications. Here, the viscosity of the coating material during the application is to be below 1000 mPas, preferably below 300 mPas (measured in a cone/plate viscometer).

25 The layer thickness of the coating material is generally 0.5 to 20 μm , in particular 1 to 10 μm , particularly preferably up to 5 μm .

The coating material is generally applied at temperatures of
30 between 0°C and 90°C, preferably 15°C and 70°C. The coating is then cross-linked by high-energy radiation such as, for example, UV radiation, electron radiation or γ -radiation. The electron radiation should have energy values of between 150 and 350 keV. Preferably, cross-linking is
35 effected by UV radiation, in particular having a wavelength of 150 to 800 nm, particularly preferably of between 200 and 450 nm. Suitable radiation sources are known to the person skilled

in the art. The intensity of radiation and the duration of the radiation depend on the processing conditions, for example, distance of the radiation source or relative movement between source and substrate. The duration, however, is generally
5 below 60 seconds, preferably between 0.001 and 30 seconds. The respective variables for the equipment can be determined by the person skilled in the art by simple adjustment.

In a particular embodiment of the process, the oxygen content
10 may be decreased in the zone above the substrate to be cross-linked. Here, it is to be in particular below 3000 ppm, preferably below 1000 ppm. This can be effected, for example, by partial or complete exchange of the ambient air present in the cross-linking zone for inert gases, for example, argon,
15 nitrogen, CO₂, or mixtures of these. An advantage of this embodiment of the process is that the required concentration of photoinitiator in the coating material can be decreased.

Another embodiment of the invention includes the additional
20 step wherein, after the application of the coating material, a film which is permeable to the high-energy radiation used is first of all applied to the substrate. It is possible to apply such a film to three-dimensional substrates, but it is preferred that the substrate be a sheet or strip. The
25 application is carried out preferably by a mechanical method; for example, the tear-resistant film can be withdrawn from a delivery roll and applied, free from voids, to the substrate surface by means of a roller. After this processing step, the coating material under the film is cross-linked by radiation.
30 An advantage of this process is that the curing takes place underneath the film under inert conditions, i.e. in particular with the exclusion of oxygen.

The film consists, for example, of polyethylene,
35 polypropylene, PET or mixtures of these. It is colored or, preferably, transparent. The film must not react with the coating material. It is tear-resistant, so that in a

subsequent processing step it can be removed from the substrate surface by drawing off. This can also be done at the premises of the end-user, so that the film can serve as protection for the object during further processing and/or
5 transport.

The use of the coating material according to the invention results in coated substrates, in particular of the metallic type, having a thin surface coating. At the same time, special
10 visual effects can be achieved such as, for example, metallic lustre, dulling, structures or colorations. Preferred uses of the objects coated according to the invention are metal sheets, metal parts or profiled metals used in architecture, for interior fittings of buildings or in furniture-making, as
15 well as metallic ornaments. In particular, the metallic workpieces coated according to the invention can be used in the manufacture of machines, articles or equipment for households, sanitary applications, hospitals as well as for the food-processing or pharmaceutical industries. For the
20 last-named fields, mainly high-grade steel is used.

The coatings according to the invention exhibit good stability and resistance to soiling by a multitude of agents of the type found, for example, in households or in the food industry,
25 such as black tea, black ink, condensed milk, fruit juices, vinegar, mustard, ketchup, mayonnaise, onions, sugar and caramel. The fingerprints which are left on uncoated metal surfaces do not leave any permanent traces on metal coated according to the invention, and can be easily removed. In
30 particular, at temperatures of up to 60°C the coatings are also resistant to acidic and alkaline cleaning agents such as, for example, rinsing agents, so-called "steel gloss" or all-purpose cleaning agents. At the same time, the visual appearance of the surface is completely preserved.

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The invention is explained in more detail by means of the following Examples, but the selection of the Examples does not

constitute a limitation to the scope of the invention. Unless otherwise specified, all quantitative data in the following Examples are per cent by weight or parts by weight, based on the total composition.

Examples

In the following coatings according to the present invention, brushed sheets of high-grade steel were used for Examples 1 to 9. Prior to being coated, all substrates were degreased by means of an aqueous, slightly alkaline cleaning agent and then dried. The components of the coating material according to the invention were homogenised by intensive mixing in high-speed stirrers. The coating material was applied in a layer weight of $< 5 \text{ g/m}^2$ by means of a roll coater or coating knife and cured in a standard atmosphere by means of UV radiation (emitter type: Fusion VPS/1 600, H-emitter, 240 W/cm, 100% performance) in a UV unit with a conveyor belt speed of 20 m/min.

The individual Examples and results are shown in Tables 1 and 2 below (quantities in parts by weight).

Table 1:

Example/RawMaterial		1	2	3	4	5	6	7	8	9
1	Aliphatic epoxy acrylate	61.9	-	-	-	-	-	-	-	-
2	Aliphatic hexa-functional urethane acrylate Mw 1000	-	56.9	56.9	56.9	-	34.0	56.9	31.5	31.6
3	Aromatic epoxy diacrylate Mw 460	-	-	-	-	80.8	37.0	-	34.3	34.5
4	Isobornyl acrylate	30.6	35.1	35.1	35.1	-	21.1	35.1	19.4	19.5
5	Neopentyl glycol propoxylate diacrylate	20.0	20.0	-	-	10.0	2.1	-	2.0	2.0
6	Vinyltrimethoxy-silane	-	-	5.0	15.0	-	-	5.0	-	-
7	Bis(gamma-trimethoxysilylpropyl)amine	10.0	10.0	-	-	4.2	1.0	-	0.9	0.8
8	Acid triacrylate (acid value 150)	2.5	3.0	3.0	3.0	-	1.8	3.0	1.7	1.7
9	Phosphoric acid acrylate (acid value 300)		-	-	-	3.0	-	-	2.8	2.8
10	Photoinitiator	5.0	5.0	5.0	5.0	5.0	3.0	4.5	4.6	4.7
11	Commercial biocide	-	-	-	-	-	-	0.5	-	-
12	Hydrophobic silica	-	-	-	-	-	-	-	2.8	-
13	Nanoparticulate Al ₂ O ₃									2.4

Photoinitiator is in the form of a 1.5:1 mixture of 1-hydroxy-1-methylethyl phenyl ketone and 1-hydroxycyclohexyl phenyl ketone.

Methods of measurement:

1. Fingerprint: a fingerprint was made on the coated metal sheet and assessed visually. It was optionally wiped off with a soft, dry cloth.
2. Cross cut in accordance with DIN 53151: cross cuts were made using a cross-hatch cutter (Erichsen Model 295) and glued over with an adhesive tape, which was then torn off and the cuts assessed. The gluing and tearing off were again carried out similarly after the cut had been exposed to steam. The cross cut test results are reported on a scale of from 0 (no additional damage except the cuts) to 5 (large sections of the coating removed from the surface).
3. Soiling: a 5 cm² area of the surface of the coated metal sheet was covered with the test agents (black tea, lemon juice, mustard, ketchup, mayonnaise) and stored for 1 hour at 60°C. The metal sheet was then rinsed with water and dried with a soft cloth.
4. Solvent resistance: a few drops of solvent were applied to the coated metal sheet and, after about 5 seconds, removed with a soft cloth. The swelling and dissolving behavior of the coating were assessed.
5. Steam test: The metal sheet bent by 90° was positioned at a small distance above a vessel filled with boiling water and there exposed to steam for 2 hours.

The results of the examinations of the surface quality and of the resistance of the coatings according to the invention are summarized in Table 2 below. The surface qualities and the scratch resistance are good; the sensitivity to fingerprints is likewise good in all the coatings according to the invention.

In the following tables, a "+" signifies that a positive or favorable result was obtained while "0" means that an intermediate (medium) result was obtained. A negative or unfavorable result (none of which were obtained in the testing

reported herein) would be signified by a “-” sign.

Table 2:

Example	Surface quality			Resistance to				
	Finger-Prints ¹	Scratch Resistance ⁶	Crosscut ²	Foods ³	Mild cleaning agents ³	Strong cleaning agents ⁷	Solvent ⁴	Steam ⁵
1	+	+	0 (0)	0	0	+	not determined	+
2	0	+	0 (0)	+	+	+	not determined	+
3	+	+	0 (0)	+	+	+	not determined	0
4	+	+	0 (0)	+	+	0	+	0
5	+	+	0 (0)	+	+	+	+	+
6	+	+	0 (1)	+	+	+	+	+
7	+	+	0 (0)	+	+	+	+	0
8	+	+	0 (0)	+	+	+	+	+
9	+	+	0 (0)	+	+	+	+	+

- 1) Visual assessment of fingerprints
- 2) Marking in accordance with DIN 53151; results after exposure to steam are shown in brackets.
- 3) Foods: mustard, tea, mayonnaise, ketchup, lemon juice, et cetera; mild cleaning agents: all-purpose cleaning agents, rinsing agents, et cetera
- 4) The tests were carried out using acetone, naphtha and ethanol.
- 5) Sample metal sheets bent by 90° were treated with steam for 2 h and assessed visually.
- 6) Determined using a hardness test rod 318, Erichsen
- 7) Cleaning agents: oven cleaner, Ceran cleaner etc.

Examples 10-12

Additional substrates were coated and tested using the coating material from Example 9:

Example	Substrate (brushed)	Layer thickness	Appearance	Cleaning agent	Finger-print
10	brass (MS 39)	5 µm	in order	+	+
11	AlMg1	5 µm	in order	+	+
12	copper	5 µm	in order	0	+